

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 March 2002 (07.03.2002)

PCT

(10) International Publication Number
WO 02/17973 A2

- (51) International Patent Classification⁷: A61L 2/00 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (21) International Application Number: PCT/GB01/03918
- (22) International Filing Date: 31 August 2001 (31.08.2001)
- (25) Filing Language: English
- (26) Publication Language: English (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (30) Priority Data:
09/653,436 1 September 2000 (01.09.2000) US
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- Published:
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 02/17973 A2

(54) Title: PREPARING STERILE ARTICLES FROM CERTAIN POLYMERS

(57) Abstract: A method of preparing a sterile article is disclosed. An article is prepared from a polymer into which is incorporated a stabilizer having the general formula: where each A is independently selected from E, OR, SR, and CO-R, and can join the aromatic ring to form an additional ring, E is R or R(OCH₂R"CH)_n, G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)(R")R'"-OR, -C(E)(R")-R'"-CO-OR, C(OE)(R")-E'"-COOR, -C(OE)R'"-O-R, -C(OE)HR, or -C(OE)R₂, J is A, each R is independently selected from H, R', R'"OR', R'"COOR', R'"C(OR)R", or R'"C(OR)R'"OR", each R' is independently selected from alkyl from C₁ to C₂₄, aryl from C₆ to C₂₄, alkaryl from C₇ to C₂₄, and aralkyl from C₇ to C₂₄, R" is H or R', R'" is alkylene from C₁ to C₂₄, arylene from C₆ to C₂₄, alkarylene from C₇ to C₂₄, or aralkylene from C₇ to C₂₄, m is 1 to 7, and n is 1 to 20. The article is exposed to gamma radiation; it yellows less after irradiation than it otherwise would.

PREPARING STERILE ARTICLES
FROM CERTAIN POLYMERS

Background of the Invention

This invention relates to the preparation of sterile articles from certain polymers. In particular, it relates to making the articles from poly(vinylchloride) (PVC) that contains a benzyl alcohol, cinnamyl alcohol, or geraniol-based stabilizer, then subjecting the article to ionizing radiation, particularly gamma radiation.

Various polymers, including PVC, polyethylene, and polypropylene, are used to make medical devices and as packaging for food. Sterilization is required and can be accomplished by exposing the devices or packages to gamma radiation. However, the gamma radiation can degrade the polymers, making them unsuitable or less acceptable for certain applications. In the case of PVC, the yellowing of sterilized articles is the most notable physical change as the result of such degradation.

Benzyl alcohol, geraniol, and some of the related ethers were reported to enhance or help enhance the thermal stability of PVC. (L. L. Wood GB 1151108, CAN 71:92299; J. D. Collins, H. Coates, I. H. Siddiqui US 3,845,017; JP 55069609 CAN 93:151163). Benzyl alcohol and cinnamyl alcohol have also been used as solvents for biocides in PVC. (EP 168949 CAN 104:187573)

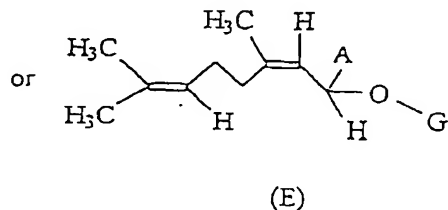
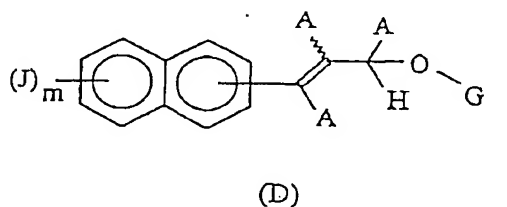
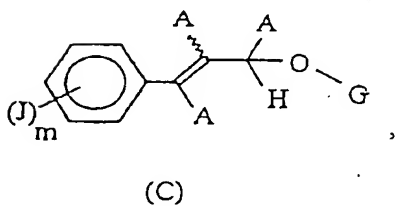
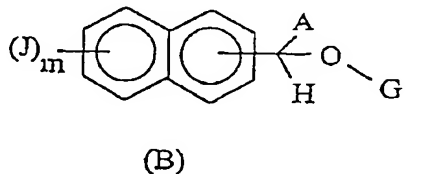
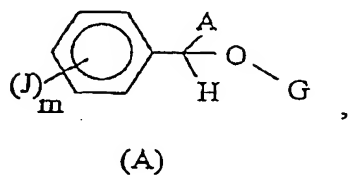
Summary of the Invention

I have discovered that when certain compounds based on benzyl alcohol, cinnamyl alcohol, or geraniol are incorporated into certain polymers and the polymers are made into articles and are sterilized with gamma radiation, substantially less yellowing occurs.

Most of the stabilizers used in this invention are FDA approved additives for food use and could be used for food and medical applications.

Description of the Preferred Embodiments

The stabilizers used in this invention have the general formula:



where each A is independently selected from E, OR, SR, and CO-R, and can join the aromatic ring to form an additional ring (e.g., α -hydroxyxanthene), E is R or $R(OCH_2R''CH)_n$, G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)(R'')R'''-OR, -C(E)(R'')R'''-CO-OR, C(OE)(R'')-E'''-COOR, -C(OE)R'''-O-R, -C(OE)HR, or -C(OE)R₂, J is A, each R is independently selected from H, R', R''OR', R'''COOR', R''C(OR'')R'', or R''C(OR'')R'''OR'', each R' is independently selected from alkyl from C₁ to C₂₄, aryl from C₆ to C₂₄, alkaryl from C₇ to C₂₄, and aralkyl from C₇ to C₂₄, R'' is H or R', R''' is alkylene from C₁ to C₂₄, arylene from C₆ to C₂₄, alkarylene from C₇ to C₂₄, or aralkylene from C₇ to C₂₄, m is 1 to 7, and n is 1 to 20. Preferably, A is H and J is R, OR, or SR as those stabilizers are easier to make and more effective. Also, R is preferably alkyl from C₇ to C₂₄, R' is preferably alkyl from C₁ to C₁₂, R'' is preferably alkyl from C₁ to C₆, R''' is preferably alkyl from C₁ to C₆, G is preferably H or benzyl, and m is preferably 1 for the same reasons. The preferred stabilizers are general formulas (A) and (C) as they are easier to make and less expensive. Example of stabilizers of formula (A) include 4-benzyloxybenzyl alcohol, benzhydrol, 9,10-dihydro-9-anthracenol, 9-hydroxyxanthene, 9H-thioxanthen-9-ol, 1,2,3,4-tetrahydro-1-naphthalenol, benzyl ether, diveratryl ether, benzyl methoxyethyl acetal, (1R)-(-)-nopol benzyl ether, 1,3-dibenzyloxy-2-propanol, benzyl benzoate, benzyl acetoacetate, benzyl phenylacetate, dibenzyl adipate, dibenzyl malonate, dibenzyl sebacate, benzyl butyl phthalate, poly(vinyl benzyl ether), poly(benzyl methacrylate), poly(methyl 4-benzyloxy-phenylsiloxane); Example of stabilizers of formula (B) include 1-naphthalenemethanol, 2-naphthalenemethanol, 1-

5 [(phenylmethoxy)methyl]naphthalene, 2-[(phenylmethoxy)-methyl]naphthalene, 1,1'-
[oxybis(methylene)]-bis-naphthalene, 2,2'-[oxybis(methylene)]-bisnaphthalene, 1-
naphthylmethyl acetate; Example of stabilizers of formula (C) include cinnamyl
alcohol, -amyl cinnamyl alcohol, trans-2-methyl-3-phenyl-2-propen-1-ol, cinnamyl
ether, benzyl cinnamyl ether, cinnamyl acetate, trans-cinnamyl butyrate, cinnamyl
benzoate, cinnamyl phenylacetate, cinnamyl isovalerate, cinnamyl acid cinnamyl
ester, poly(vinyl cinnamyl ether), poly(cinnamyl methacrylate), poly(methyl 4-
cinnamyloxy-phenylsiloxane); Example of stabilizers of formula (D) include 3-(1-
10 naphthyl)-2-propen-1-ol, 3-(2-naphthyl)-2-propen-1-ol, 3-(1-naphthalenyl)-2-propen-
1-ol acetate, 3-(2-naphthalenyl)-2-propen-1-ol acetate; Example of stabilizers of
formula (E) include geraniol, benzyl geranyl ether, geranyl hexanoate, geranyl
phenylacetate, poly(vinyl geranyl ether), poly(geranyl methacrylate), poly(methyl 4-
geranyloxy-phenylsiloxane).

15 Some of the stabilizers are commercially available as food additives. Those
that are not commercially available can be made by techniques known in the art. For
example, cinnamyl benzyl ether can be made by the benzylation of cinnamyl alcohol
with benzyl chloride or benzyl bromide in the presence of a base.

20 The stabilizers of this invention are effective in reducing the yellowing of
articles made from polymers such as PVC, polyvinylidene chloride, polyethylene, and
polypropylene after exposure to ionizing radiation. The polymer can be made into
any type of article, including medical devices, food packaging, and radiation
protection devices.

The polymer can be stabilized by the addition of about 0.005 to about 70 phr (parts by weight per 100 part by weight of the polymer) of the stabilizer to the polymer. Less stabilizer is less effective and more stabilizer offers little additional benefit. The preferred amount of stabilizer is about 0.2 to about 20 phr. The stabilizer can be added to a polymer in a variety of ways, such as mixing the reactants at the beginning or during polymerization. The stabilizer is preferably added after at least 70 wt% of the monomer has polymerized. The stabilizer can be added as a solid or with a solvent as a slurry or a solution. Common organic solvents such as N-methylpyrrolidone, diglyme, acetamide, acetone, methanol, ethanol, isopropanol, dimethylsulfoxide, or dimethylformamide can be used; water can also be used. Water miscible solvents, such as acetone, tetrahydrofuran, and methanol, are preferred. If the stabilizer is a solid, it is preferable to add it in a solvent as that achieves a more uniform distribution of the stabilizer in the polymer. The stabilizer can also be added to the polymer along with or as a shortstop, or during the drying or compounding of the polymer. Various methods can be used for compounding, including milling, dry mixing, and extrusion.

The following examples further illustrate this invention:

EXAMPLES 1 to 125

To a mixture of 150.00 g PVC (sold by Occidental Chemical Corporation as "Oxy 240" or sold by Oxy Vinyls as "OV 30"), 0.30 g stearic acid (used as a lubricant), 0.23 g of a zinc and calcium mixed salts of mixed fatty acids (used as a

heat stabilizer; sold by Witco as "Mark 152 S"), 97.50g (less the amount of gamma ray stabilizer used) of dioctyl phthalate ("DOP," used as a plasticizer and to increase flexibility), 15.00 g epoxidized soy bean oil (used as an HCl scavenger to reduce degradation; sold by Witco as "Drapex 6.8"), was added a gamma ray stabilizer. The mixture was thoroughly blended and hot milled at 300°F (182°C) for 5 minutes. The resulting PVC sheet was cut and pressed into a 4"x3"x1/4" (10x8x0.6 cm) plaque at 330°F (182°C). The plaque was divided into two smaller pieces. One was saved for comparison and one was subjected to γ radiation at a dose of 50 kGy. The irradiated piece was again divided into two pieces and one of these pieces was oven aged at 50°C for 48 hours. All of the samples were measured for yellowness index with a Macbeth 2020 Plus Color Eye Spectrometer, as described by the Hunter equations (see "The Measurement of Appearance" by Richard S. Hunter, John Wiley & Sons, New York, 1975). The following table gives the stabilizers used and the results.

| Example | Stabilizer | Amount (g) | Yellowness | | |
|---------|----------------------------|------------|------------|-----------------|-------------|
| | | | Initial | After Radiation | After Aging |
| Control | none | none | 19.1 | 55.4 | 79.9 |
| 1 | Benzyl ether | 0.5 | 16.2 | 42.9 | 65.1 |
| 2 | " | 1.0 | 17.0 | 37.0 | 57.2 |
| Control | none | none | 21.1 | 57.2 | 77.2 |
| 3 | Benzyl ether | 2.01 | 32.8 | 33.1 | 51.9 |
| 4 | " | 5.02 | 19.4 | 26.9 | 42.4 |
| 5 | " | 10.02 | 17.6 | 22.3 | 36.5 |
| 6 | " | 15.04 | 15.6 | 19.7 | 32.2 |
| 7 | " | 20.03 | 16.1 | 18.8 | 31 |
| 8 | " | 30.02 | 15.4 | 17.3 | 27.5 |
| Control | none | none | 17.1 | 52.3 | 84.4 |
| 9 | Benzyl methoxyethyl acetal | 0.5 | 17.9 | 42.1 | 66.1 |
| 10 | " | 1.02 | 16.8 | 35.1 | 58.9 |
| 11 | " | 1.5 | 16.5 | 34.6 | 54.5 |

| | | | | | |
|---------|-----------------------------|-------|------|------|------|
| 12 | " | 2.02 | 15.4 | 29.7 | 50.5 |
| 13 | " | 2.52 | 17.2 | 27.8 | 47.8 |
| 14 | " | 3.02 | 16.5 | 27.5 | 45.2 |
| Control | none | none | 19.3 | 55.7 | 75.4 |
| 15 | Diveratryl ether | 1.30 | 19.2 | 39.8 | 59.7 |
| 16 | " | 3.50 | 20.6 | 33.2 | 50.8 |
| 17 | Benzyl cinnamyl ether | 2.00 | 18.9 | 35.8 | 47.9 |
| 18 | " | 4.00 | 17.1 | 30.5 | 37.8 |
| 19 | " | 6.00 | 16.1 | 27.4 | 36.4 |
| Control | none | none | 19.1 | 55.4 | 79.9 |
| 20 | (1R)-(-)-Nopol benzyl ether | 6.46 | 19.3 | 38.6 | 54.7 |
| 21 | " | 12.92 | 16.7 | 34.8 | 47.0 |
| Control | none | none | 19.1 | 55.4 | 79.9 |
| 22 | 1,3-Dibenzoyloxy-2-propanol | 0.51 | 17.5 | 49.3 | 70.7 |
| 23 | " | 1.02 | 16.6 | 44.4 | 64.3 |
| 24 | " | 1.54 | 17.5 | 42.8 | 62.4 |
| 25 | " | 2.03 | 17.4 | 39.8 | 60.3 |
| Control | none | none | 18.1 | 50.2 | 75.5 |
| 26 | 4-Benzyloxybenzyl alcohol | 2.40 | 18.6 | 28.4 | 42.1 |
| 27 | " | 4.80 | 18.1 | 25.5 | 34.7 |
| Control | none | none | 19.1 | 55.4 | 79.9 |
| 28 | 9-Hydroxyxanthene | 0.50 | 17.1 | 62.9 | 84.2 |
| 29 | " | 1.00 | 18.4 | 51.4 | 72.7 |
| 30 | " | 1.52 | 17.3 | 46.7 | 68.4 |
| 31 | " | 2.17 | 17.7 | 42.2 | 63.7 |
| Control | none | none | 21.1 | 57.2 | 77.2 |
| 32 | Benzyl benzoate | 2.01 | 18.6 | 45.7 | 65.3 |
| 33 | " | 5.1 | 19.0 | 39.7 | 58.5 |
| 34 | " | 10.01 | 18.7 | 34.3 | 51.8 |
| 35 | " | 15.03 | 18.1 | 29.9 | 47.2 |
| 36 | " | 20.19 | 18.9 | 31.7 | 50.5 |
| 37 | " | 30.08 | 19.1 | 28.3 | 43.8 |
| Control | none | none | 19.1 | 55.4 | 79.9 |
| 38 | benzyl acetoacetate | 4.88 | 17.9 | 34.1 | 46.1 |
| 39 | " | 9.72 | 23.0 | 31.0 | 42.4 |
| Control | none | none | 21.1 | 57.2 | 77.2 |
| 40 | Dibenzyl malonate | 2.70 | 16.9 | 29.4 | 45.3 |
| 41 | " | 6.43 | 17.8 | 30.8 | 48.6 |
| Control | none | none | 19.3 | 55.7 | 75.4 |
| 42 | Dibenzyl sebacate | 3.05 | 18.8 | 39.9 | 59.4 |
| 43 | " | 6.06 | 18.5 | 34.2 | 52.1 |
| 44 | " | 9.08 | 17.7 | 33.1 | 48.8 |
| Control | none | none | 19.3 | 55.7 | 75.4 |

| | | | | | |
|---------|---------------------------------------|--------|------|------|------|
| 45 | Dibenzyl adipate | 3.00 | 18.0 | 40.0 | 58.3 |
| 46 | " | 6.01 | 17.9 | 35.3 | 52.8 |
| 47 | " | 9.02 | 21.1 | 32.0 | 47.8 |
| Control | none | none | 19.3 | 55.7 | 75.4 |
| 48 | Benzyl butyl phthalate | 10.03 | 18.0 | 40.2 | 60.7 |
| 49 | " | 20.03 | 18.1 | 35.8 | 53.7 |
| 50 | " | 30.05 | 18.8 | 32.5 | 48.3 |
| 51 | " | 40.04 | 18.5 | 32.0 | 46.6 |
| 52 | " | 50.02 | 18.7 | 30.6 | 45.0 |
| 53 | " | 60.06 | 20.1 | 29.2 | 43.6 |
| Control | none | none | 17.1 | 52.3 | 84.4 |
| 54 | Dibenzyl phthalate | 1.50 | 17.7 | 54.3 | 80.4 |
| 55 | " | 4.29 | 15.0 | 47.7 | 70.9 |
| Control | none | none | 17.1 | 52.3 | 84.4 |
| 56 | Cinnamyl alcohol | 0.54 | 17.0 | 37.6 | 62.5 |
| 57 | " | 1.11 | 14.7 | 27.6 | 48.4 |
| 58 | " | 1.53 | 17.2 | 27.5 | 42.8 |
| 59 | " | 2.03 | 15.5 | 21.9 | 35.9 |
| 60 | " | 2.6 | 16.9 | 23.6 | 34.7 |
| 61 | " | 3.09 | 14.6 | 20.0 | 31.5 |
| Control | none | none | 17.1 | 52.3 | 84.4 |
| 62 | Alpha-amyl cinnamyl alcohol | 0.51 | 18.7 | 56.9 | 77.3 |
| 63 | " | 1.01 | 18.0 | 57.1 | 77.1 |
| 64 | " | 1.5 | 17.6 | 57.6 | 74.2 |
| 65 | " | 2.01 | 18.9 | 59.0 | 74.7 |
| 66 | " | 2.5 | 19.3 | 57.7 | 72.8 |
| 67 | " | 3.02 | 18.9 | 57.2 | 70.0 |
| Control | none | none | 16.9 | 61.7 | 84.1 |
| 68 | Trans-2-methyl-3-phenyl-2-propen-1-ol | 1.01 | 17.3 | 34.8 | 55.4 |
| 69 | " | 2.00 | 14.4 | 27.8 | 44.0 |
| 70 | " | 3.00 | 16.3 | 24.2 | 37.8 |
| Control | none | none | 19.3 | 55.7 | 75.4 |
| 71 | Cinnamyl ether | 1.0205 | 19.7 | 44.1 | 55.9 |
| 72 | " | 2.0412 | 20.7 | 37.1 | 46.4 |
| 73 | " | 3.0637 | 18.8 | 33.1 | 41.9 |
| 74 | " | 5.1007 | 18.8 | 29.0 | 36.3 |
| 75 | " | 8.1642 | 18.2 | 29.2 | 37.3 |
| Control | none | none | 19.3 | 55.7 | 75.4 |
| 76 | Cinnamyl acetate | 1.39 | 19.7 | 39.6 | 51.1 |
| 77 | " | 3.30 | 19.3 | 36.8 | 51.6 |
| Control | none | none | 16.6 | 49.1 | 52.5 |
| 78 | Trans-cinnamyl butyrate | 1.00 | 18.2 | 40.2 | 46.5 |

| | | | | | |
|---------|------------------------------|------|------|------|------|
| 79 | " | 2.02 | 17.5 | 35.5 | 38.7 |
| 80 | " | 3.00 | 17.4 | 37.3 | 37.5 |
| 81 | " | 4.01 | 17.0 | 33.9 | 38.1 |
| 82 | " | 5.01 | 16.5 | 33.2 | 36.3 |
| 83 | " | 6.02 | 16.0 | 32.8 | 34.3 |
| Control | none | none | 19.3 | 61.6 | 79.0 |
| 84 | Cinnamyl benzoate | 3.03 | 18.8 | 52.2 | 64.4 |
| 85 | " | 6.00 | 18.5 | 44.0 | 56.5 |
| 86 | " | 9.02 | 18.6 | 42.1 | 52.8 |
| Control | none | none | 19.3 | 61.6 | 79.0 |
| 87 | Cinnamyl phenylacetate | 3.01 | 18.3 | 43.8 | 56.9 |
| 88 | " | 6.02 | 18.7 | 39.5 | 49.7 |
| 89 | " | 9.04 | 18.7 | 36.4 | 46.8 |
| Control | none | none | 19.3 | 61.6 | 79.0 |
| 90 | Trans-cinnamyl isovalerate | 3.01 | 18.6 | 47.6 | 58.5 |
| 100 | " | 6.01 | 18.5 | 42.7 | 52.6 |
| 101 | " | 9.01 | 18.7 | 39.6 | 49.1 |
| Control | none | none | 19.3 | 55.7 | 75.4 |
| 102 | Cinnamic acid cinnamyl ester | 3.03 | 18.7 | 42.6 | 52.0 |
| 103 | " | 6.04 | 19.3 | 38.3 | 45.9 |
| 104 | " | 9.05 | 19.3 | 35.9 | 45.1 |
| Control | none | none | 14.9 | 54.0 | 74.7 |
| 105 | Geraniol | 0.49 | 14.2 | 48.1 | 67.5 |
| 106 | " | 0.99 | 15.0 | 37.7 | 56.6 |
| 107 | " | 2.10 | 14.4 | 32.9 | 50.4 |
| 108 | " | 2.99 | 15.1 | 31.2 | 45.1 |
| Control | none | none | 17.1 | 52.3 | 84.4 |
| 109 | Geranyl hexanoate | 0.51 | 15.6 | 46.0 | 72.0 |
| 110 | " | 1.01 | 17.5 | 45.2 | 73.3 |
| 111 | " | 1.52 | 14.8 | 42.5 | 70.7 |
| 112 | " | 2.02 | 18.6 | 42.2 | 67.8 |
| 113 | " | 2.5 | 15.2 | 36.3 | 66.2 |
| 114 | " | 3.03 | 17.3 | 37.9 | 67.8 |
| Control | none | none | 16.6 | 49.1 | 51.5 |
| 115 | Geranyl benzyl ether | 1.03 | 15.5 | 36.2 | 44.7 |
| 116 | " | 2.01 | 15.0 | 33.3 | 35.1 |
| 117 | " | 3.00 | 14.2 | 26.7 | 33.2 |
| 118 | " | 4.00 | 14.2 | 26.1 | 33.2 |
| 119 | " | 5.01 | 14.7 | 23.4 | 35.1 |
| 120 | " | 6.04 | 15.6 | 25.2 | 32.0 |
| Control | none | none | 16.6 | 49.1 | 52.5 |
| 121 | Geranyl phenylacetate | 1.50 | 18.4 | 40.5 | 47.3 |
| 122 | " | 3.00 | 15.7 | 35.1 | 40.2 |

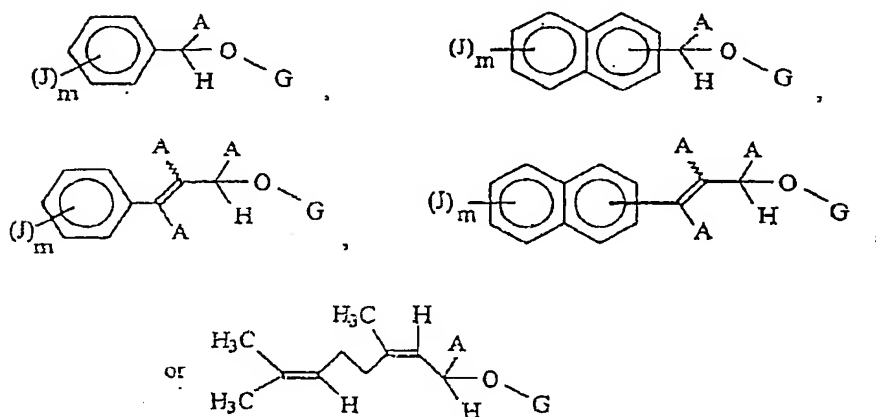
| | | | | | |
|-----|---|------|------|------|------|
| 123 | " | 4.50 | 16.2 | 29.9 | 35.5 |
| 124 | " | 6.02 | 15.3 | 30.2 | 37.3 |
| 125 | " | 7.52 | 16.0 | 31.2 | 33.5 |

5 As can be observed from the above table, after γ radiation the polymers that contained a stabilizer had significantly less discoloration than the control samples. The table also shows that ethers and alcohols are better at reducing yellowing than esters and can be used in lower amounts.

CLAIMS:

1. A method of preparing a sterile article comprising

- (A) producing a polymer selected from the group consisting of poly(vinyl chloride), poly(vinylidene chloride), polyethylene, and polypropylene, that contains about 0.005 to about 70 phr of a stabiliser having the general formula:



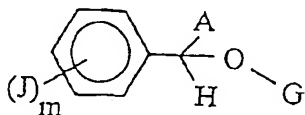
where each A is independently selected from E, OR, SR and CO-R, and can join the aromatic ring to form an additional ring, E is R or R(OCH₂R''CH)_n, G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)R''R'''-OR, -C(E)(R'')-R'''-CO-OR, C(OE)(R'')-E'''-COOR, -C(OE)R'''-O-R, -C(OE)HR, or -C(OE)R₂, J is A, each R is independently selected from H, R', R''OR', R'''COOR', R'''C(OR'')R'', or R'''C(OR'')R'''OR'', each R' is independently

selected from alkyl from C₁ to C₂₄, alkaryl from C₇ to C₂₄, and aralkyl from C₇ to C₂₄, R'' is H or R', R'' is alkylene from C₁ to C₂₄, arylene from C₆ to C₂₄, alkarylene from C₇ to C₂₄, or aralkylene from C₇ to C₂₄, m is 1 to 7, and n is 1 to 20;

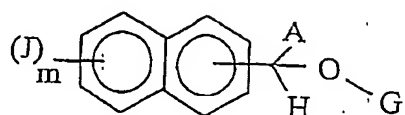
(B) making said article from said polymer, and

(C) sterilising said article with ionising radiation.

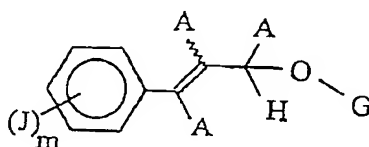
2. A method according to Claim 1 wherein said polymer comprises poly(vinylchloride).
3. A method according to Claim 1 or 2 wherein A is H.
4. A method according to Claim 1, 2 or 3 wherein G is H or benzyl.
5. A method according to any one of Claims 1 to 4 wherein J is R, OR, or SR.
6. A method according to any one of claims 1 to 5 wherein R is alkyl from C₇ to C₂₄.
7. A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula



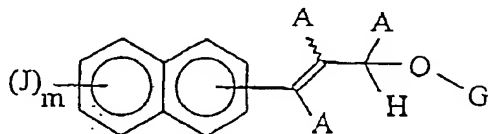
8. A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula



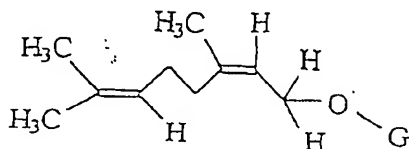
9. A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula



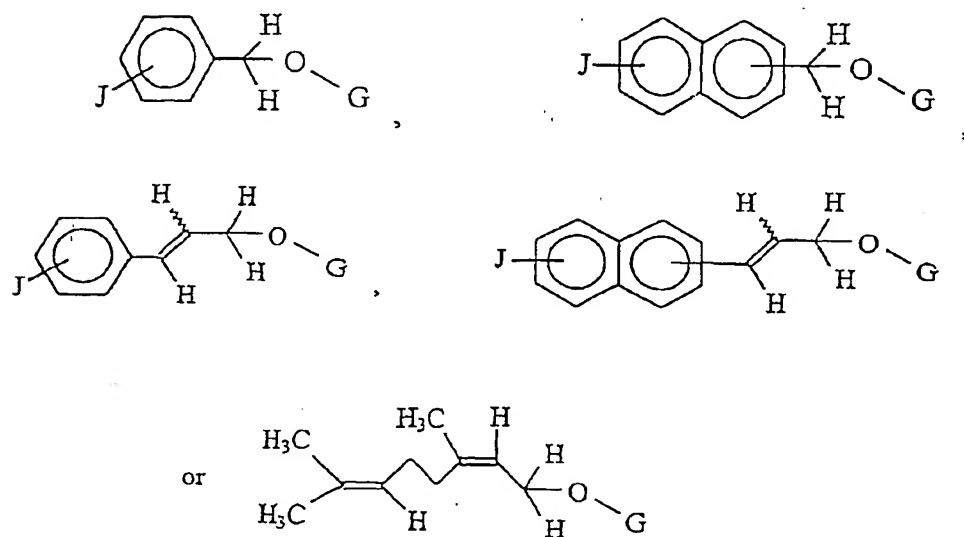
10. A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula



11. A method according to any one of Claims 1 to 6 wherein said stabiliser has the general formula



12. A sterile article prepared according to the method of any one of Claims 1 to 11.
13. A method preparing a sterile article comprising
- (A) making poly(vinyl chloride) that contains about 0.2 to about 20 phr of a stabiliser having the general formula

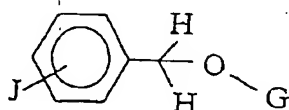


where G is H or benzyl and J is R, OR, or SR, and R is alkyl from C₇ to C₂₄.

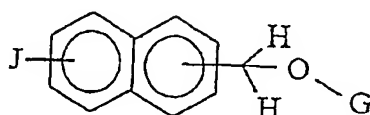
- (B) making said article from said poly(vinyl chloride), and

(C) sterilising said article with gamma radiation.

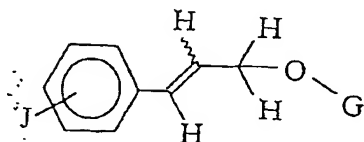
14. A method according to Claim 13 wherein said stabiliser has the formula



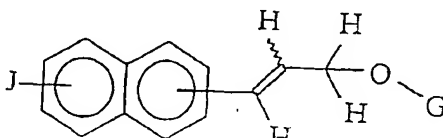
15. A method according to Claim 13 wherein said stabiliser has the general formula



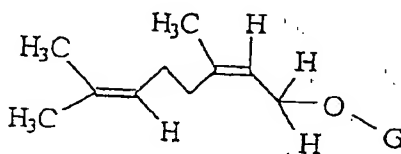
16. A method according to Claim 13 wherein said stabiliser has the general formula



17. A method according to Claim 13 wherein said stabiliser has the general formula



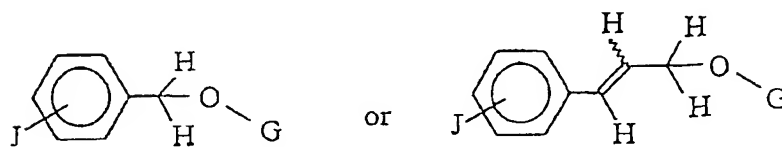
18. A method according to Claim 13 wherein said stabiliser has the general formula



19. A sterile medical article prepared according to the method of any one of Claims 13 to 18.

20. A method of preparing a sterile medical article comprising

- (A) making poly(vinyl chloride) that contains about 0.2 to about 20 wt % of a stabiliser having the general formula

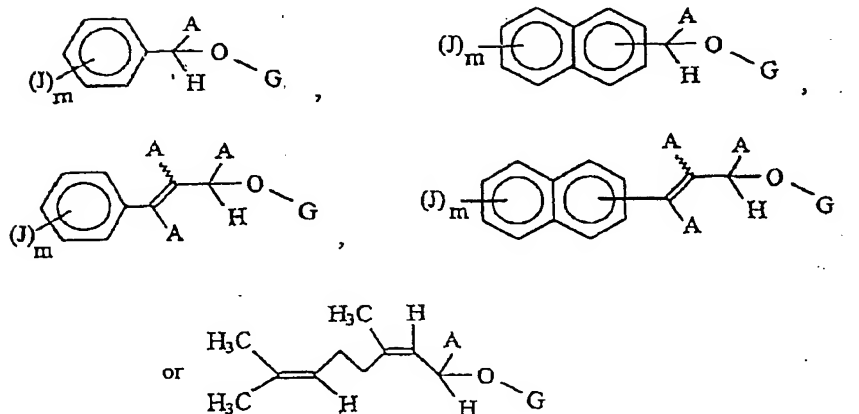


where G is H or benzyl and each R is independently selected from alkyl from C₈ to C₁₂.

- (B) making said medical article from said poly(vinyl chloride), and
(C) sterilising said medical article with gamma radiation.

21. A resin comprising

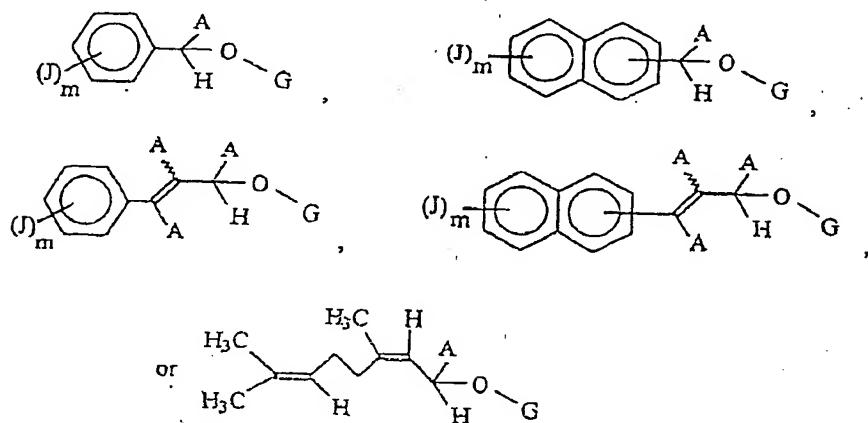
- (A) a polymer selected from the group consisting of poly(vinyl chloride), poly(vinylidene chloride), polyethylene and polypropylene that contains about 0.005 to about 70 phr of a stabiliser having the general formula



where each A is independently selected from E, OR, SR, and CO-R, and can join the aromatic ring to form an additional ring, E is R or $R(OCH_2R''CH)_n$, G is E, CO-R, $-C(E)H-O-R$, $C(OE)(H)-O-R$, $-C(E)(R'')R'''-OR$, $-C(E)(R'')-R'''-CO-OR$, $C(OE)(R'')-E'''-COOR$, $-C(OE)R'''-O-R$, $-C(OE)HR$, or $-C(OE)R_2$, J is A, each R is independently selected from H, R' , $R'''OR'$, $R'''COOR'$, $R'''C(OR'')R''$, or $R'''C(OR'')R'''OR''$, each R' is independently selected from alkyl from C_1 to C_{24} , aryl from C_6 to C_{24} , and alkaryl from C_7 to C_{24} , R'' is H or R' , R''' is alkylene from C_1 to

C_{24} , arylene from C_6 to C_{24} , alkarylene from C_7 to C_{24} , or aralkylene from C_7 to C_{24} , m is 1 to 7, and n is 1 to 20.

22. A stabiliser for use in stabilising a polymer, the stabiliser having the general formula



where each A is independently selected from E , OR , SR and $CO-R$, and can join the aromatic ring to form an additional ring, E is R or $R(OCH_2R''CH)_n$, G is E , $CO-R$, $-C(E)H-O-R$, $C(OE)(H)-O-R$, $-C(E)R''R'''-OR$, $-C(E)(R'')-CO-OR$, $C(OE)(R'')-E'''-COOR$, $-C(OE)R'''-O-R$, $-C(OE)HR$, or $-C(OE)R_2$, J is A , each R is independently selected from H , R' , $R''OR'$, $R''COOR'$, $R''C(OR'')R''$, or $R''C(OR'')R'''OR''$, each R' is independently selected from alkyl from C_1 to C_{24} aryl from C_6 to C_{24} , and aralkyl

from C₇ to C₂₄, R'' is H or R', R'' is alkylene from C₁ to C₂₄,
arylene from C₆ to C₂₄, alkarylene from C₇ to C₂₄ or aralkylene
from C₇ to C₂₄, m is 1 to 7, and n is 1 to 20;

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



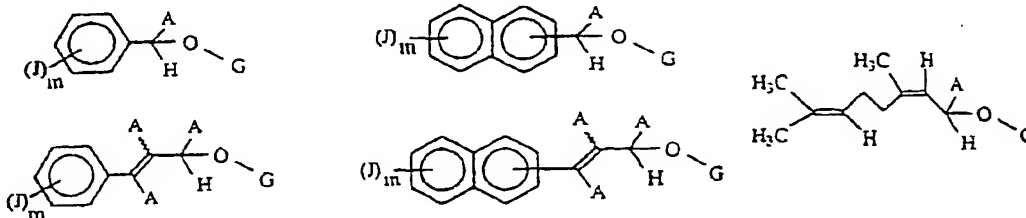
(43) International Publication Date
7 March 2002 (07.03.2002)

PCT

(10) International Publication Number
WO 02/17973 A3

- (51) International Patent Classification⁷: C08K 5/04, (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (21) International Application Number: PCT/GB01/03918
- (22) International Filing Date: 31 August 2001 (31.08.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 09/653,436 1 September 2000 (01.09.2000) US
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- (74) Agent: FRANKLAND, Nigel, H.; Forrester Ketley & Co., Forrester House, 52 Bounds Green Road, London N11 2EY (GB).
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- (88) Date of publication of the international search report: 13 June 2002
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PREPARING STERILE ARTICLES FROM CERTAIN POLYMERS



(57) Abstract: A method of preparing a sterile article is disclosed. An article is prepared from a polymer into which is incorporated a stabilizer having the general formula: where each A is independently selected from E, OR, SR, and CO-R, and can join the aromatic ring to form an additional ring, E is R or R(OCH₂R'^{''}CH)_n, G is E, CO-R, -C(E)H-O-R, C(OE)(H)-O-R, -C(E)(R'')R'-OR, -C(E)(R'')-R'-CO-OR, C(OE)(R'')-E'-COOR, -C(OE)R'-O-R, -C(OE)HR, or -C(OE)R₂, J is A, each R is independently selected from H, R', R''OR', R''COOR', R''C(OR'')R'', or R''C(OR'')R''OR'', each R' is independently selected from alkyl from C₁ to C₂₄, aryl from C₆ to C₂₄, alkaryl from C₇ to C₂₄, and aralkyl from C₇ to C₂₄, R'' is H or R', R''' is alkylene from C₁ to C₂₄, arylene from C₆ to C₂₄, alkarylene from C₇ to C₂₄, or aralkylene from C₇ to C₂₄, m is 1 to 7, and n is 1 to 20. The article is exposed to gamma radiation:

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 01/03918

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/04 C08L27/06 A61L2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

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Date of the actual completion of the international search

5 April 2002

Date of mailing of the international search report

16/04/2002

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2260 HV Rijswijk

Authorized officer

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/03918

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
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